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(54) Title: A PROCESS FOR BLEACHING A LIGNOCELLULOSIC PULP

(57) Abstract: The invention relates to improvements in the bleaching of a lignocellulosic pulp by adding carbon dioxide to provide a beneficial pH profile in the chlorine dioxide bleaching or delignification. The resulting bleached pulp is used in the production of paper or pulp. The invention also relates to the use of carbon dioxide for providing a desired pH profile in a chlorine dioxide bleaching stage.



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A process for bleaching a lignocellulosic pulp

The present invention relates to improvements in the chlorine dioxide bleaching of a lignocellulosic pulp. The invention specifically relates to providing a beneficial pH profile in the chlorine dioxide bleaching or delignification at a pulp mill. The resulting bleached pulp is used in the production of paper or market pulp. The invention also relates to the use of carbon dioxide for providing a desired pH profile in a chlorine dioxide bleaching stage.

Elemental chlorine free (ECF) bleaching processes have gained ground for the production of bleached chemical pulp at the expense of classic chlorine bleaching. The most important factors behind this development are that bleached pulp of a high quality can be produced with an acceptable potential environmental impact. Furthermore, chlorine dioxide is well established in the pulp industry. ECF bleaching means that elemental or molecular chlorine, Cl_2 , is ruled out and the bleaching processes are based on chlorine dioxide in combinations with e.g. oxygen, hydrogen peroxide, ozone and peracetic acid in different bleaching stages.

Examples of ECF bleaching sequences are D(EO)D(EP)D and ODQ(PO), where D denotes a chlorine dioxide stage, O oxygen, P hydrogen peroxide, E sodium hydroxide (alkaline extraction) and Q a chelating stage. Bleaching chemicals within parentheses are used together. Thus, (EO) means an oxygen reinforced alkaline extraction stage and (PO) a peroxide stage with addition of oxygen. Washing of the pulp is normally applied after each bleaching stage.

A drawback associated with chlorine dioxide is the relatively high cost, the high power consumption in the production of chlorine dioxide via intermediate sodium chlorate and the generation of chloride ions in the spent bleach liquors. Systems closure, i.e. the recycling of spent bleaching liquors to the closed part of the pulp mill, becomes difficult due to the presence of chloride.

The first bleaching stage with chlorine dioxide after cooking and optionally oxygen delignification is often denoted D0. The D0 stage can be followed by an alkaline extraction stage, e.g. an (EO) stage, which in turn can be followed by another chlorine dioxide stage which then is denoted D1. A bleaching sequence comprising three chlorine

dioxide stages after oxygen delignification is then abbreviated according to OD0(E0)D1(EP)D2.

Besides process parameters such as pulp consistency, temperature and charge of chlorine dioxide, pH has a strong influence on the brightness increase and the degradation of the polysaccharides during chlorine dioxide bleaching. The normal practice is to adjust the pH of the pulp suspension through addition of acid or alkali before chlorine dioxide is added. When the chlorine dioxide solution is added to a neutral or weakly alkaline pulp suspension, the pH drops rapidly during the time it takes to mix the bleaching chemical with the pulp suspension and the initial bleaching reactions take place. The mixing is typically completed in less than a minute by means of high shear mixers. After the rapid initial change, the pH remains at a relatively stable level with a small decrease during the course of the bleaching. The decrease in pH is caused by acidic reaction products which are formed when the pulp components react with the chlorine dioxide.

The initial pH adjustment is normally made in such a way that the end-pH is below or within a certain range, typically pH 2.5 to 4.5 depending on the position of the chlorine dioxide stage in the bleaching sequence. If the pH is kept at too high a level by improper control, the desired bleaching reactions do not take place and a large portion of the added chlorine dioxide remains unreacted after the bleaching. According to Reeve et al. (Reeve, D.W., Weishar, K.M.; 1990 Annual Meeting, proceedings Tappi Press, Atlanta 1990) addition of acid is required if the pH is above 3 before the D0 stage.

Dahl et al. (Dahl, O., Niimäki, J., Tirri, T., Kuopanportti, H., Paperi Puu 79 (1997):8, 560) have demonstrated that the higher the chlorine dioxide charge is, the lower is the optimum end-pH and the later in the bleaching sequence the chlorine dioxide stage is placed, the higher is the optimum end-pH. Dahl et al. (1997) report that the lowest kappa number in the D0 stage, measured after the first alkali stage, was achieved at final pH values of 2.0 to 3.5 depending on the charge of chlorine dioxide. The pulp was an oxygen delignified softwood kraft pulp. In the D1 stage, they found the optimum pH range to be 3.0 to 4.0 with regard to brightness. Correspondingly, the optimum pH range in the D2 stage was 4.0 to 5.0.

Chlorine dioxide is involved in several equilibria, which are influenced by pH. When chlorine dioxide reacts with pulp under acidic conditions, chlorous acid, HClO_2 , and hypochlorous acid, HOCl , are formed in a series of step-wise reactions. Chlorine dioxide is also converted to chlorate and chloride in proportions that are dependent on pH. Chlorate and chloride as such do not have any bleaching effect. Seger et. al. (Seger, G.,

Jameel, H., Chang, H.-m., Tappi J. 75(1992):7, 174) and Yoon et al. (Yoon, B.-H., Kim, G.-S., Wang, L.-J., 9th ISWPC, Montreal, Quebec, June 1997, poster session, proceedings p. 128-1 to 28-5) have investigated how the efficiency of chlorine dioxide bleaching can be improved by applying a two-step pH process.

The two-step process according to Seger et al. (1992) is performed by first adding sodium hydroxide to the pulp, then the pulp is mixed with chlorine dioxide and the bleaching reactions take place at a high pH. When the first step is completed after 5 to 15 minutes with an optimum end pH of 6.0 to 7.5, acid is added to reach a pH of 1.7 to 4.4 to complete the bleaching for 2.5 h or longer.

According to Seger et al. (1992), the two-step process produced the best results when it was applied in a D1 stage in a sequence of the type CED1ED2 or (C+D)ED1ED2, where C denotes a chlorine stage and (C+D) a chlorine stage with addition of chlorine dioxide. With the two-step process, a higher brightness for a certain charge of chlorine dioxide was attained compared with a conventional D1 stage. They also noted that the high/low-pH process was not effective on pulps with kappa numbers above 10. Thus for a D0(EO)D1 sequence with application of the high/low-pH process in the D0 stage on a pulp with a kappa number above 10 they found that it performed no better, and was sometimes even less effective, than a conventional D stage. It should be noted that the conditions applied by Seger et al. in the chlorine dioxide stages with two pH levels were a total treatment time of 3 h at 70 °C.

Yoon et al. (1997) applied a similar dual pH treatment in D1 stages in sequences of the type CED1ED2 or (C+D)ED1ED2. During the first step the pH was kept at 7.0 for 5 to 20 minutes and then followed the second step during which the pH was kept at 4.0 for 160 to 175 minutes. The temperature in the high/low-pH D1 stage was 70 °C. They report a higher brightness for the dual pH treatment compared with a conventional single treatment.

Teder et al. (Teder, A., Tormund, D., Tappi 62(1978): 12, 59-62) studied the influence of different variables in chlorine dioxide bleaching by means of a flow-through reactor. The experiments were carried out in a D1 stage at a low pulp consistency (0.4%) and bleach liquor of constant compositions was pumped through the reactor during each experiment. The authors tested the effect of a dual high/low pH on the bleaching and found that a pretreatment at a high pH of about pH 6 provided some decrease in the viscosity drop of the pulp. The high pH period could be prolonged by an addition of sodium bicarbonate or sodium hydroxide.

In order to obtain the two-step pH treatment the pulp has to be treated with a pH adjusting compound at two separate points of time, i.e. first the initial high pH is provided by an alkaline compound and after the desired reaction time at the high pH an acid has to be added to the pulp to lower the pH to the desired low pH value. However, achieving such a second acid treatment in an industrial bleaching plant poses several technical difficulties.

Adding an acid to the pulp at a subsequent step after the bleaching has started requires the existence of a second inlet and a second mixer to properly mix the acid into the suspension in the bleaching apparatus and a second reactor to provide the required retention time.

It is an object of the present invention to provide a high/low pH treatment in a chlorine dioxide stage without the drawbacks of the prior art processes.

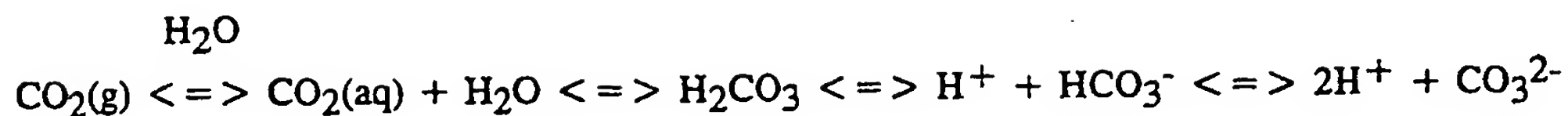
The object of the invention is thus to provide a novel procedure for causing chlorine dioxide bleaching at different pH values without the need for addition of an acid at a later stage in the proceedings.

Another object of the present invention is to provide an self-regulating pH control of the pulp during the initial stage of a chlorine dioxide bleaching.

Specifically the present invention aims at providing an advantageous pattern of pH adjustment, i.e. a pH profile which includes the advantages of a treatment at a high pH with the advantages of a treatment at a low pH.

The present invention is based on the realization that carbon dioxide can be used in a chlorine dioxide bleaching stage to provide a self-regulating buffering system capable of providing an initial bleaching at a high pH and a final bleaching at a low pH. Because of the self-regulating buffering system there will be no need of adding an acid after the initial high pH period. Due to the introduction of carbon dioxide, a self-regulating two-step pH profile is obtained.

Carbon dioxide is a gas, which dissolves under alkaline conditions, e.g. in water or a pulp suspension, forming carbonic acid, H_2CO_3 , which readily dissociates and acts as a pH decreasing agent:



(g = gas; aq = dissolved in water)

The carbonic acid produced by the dissolving carbon dioxide is a weak acid and it dissociates in an alkaline environment forming bicarbonate and carbonate ions. However, as the pH decreases, the equilibrium is pushed back towards the initial reaction stage and carbon dioxide in a dissolved state is formed. Finally, carbon dioxide in gaseous form is recreated. The bicarbonate ions have a strong buffering action striving to keep the pH in the neutral or slightly alkaline pH range. However, when the pH decreases, the dissociation tendency of the carbonic acid is reduced and finally the carbon dioxide, capable of leaving the system, is regenerated.

The self-adjusting buffering system created by the introduction of carbon dioxide into the chlorine dioxide bleaching stage in accordance with the present invention has been found to provide unexpected advantages to the bleaching result.

Consequently, the present invention, which is defined in the appended claims, concerns a process for bleaching a lignocellulosic pulp with chlorine dioxide in an aqueous suspension at different pH values. The process comprises the following steps: providing an aqueous lignocellulosic pulp suspension in a first chlorine dioxide bleaching stage after cooking; adding carbon dioxide to said lignocellulosic pulp; subsequently adding a chlorine dioxide bleaching agent to said lignocellulosic pulp suspension. The carbon dioxide is added for providing in said suspension a buffering system capable of retarding the decrease in the pH of said cellulosic pulp suspension after said addition of chlorine dioxide in order to provide an initial chlorine dioxide bleaching period at a $\text{pH} \geq 4.5$, the buffering capacity of said system being consumed after said initial period by acidic reaction products generated in said suspension and causing the pH to drop to a value below 4.5 after said initial period. Subsequently, said chlorine dioxide bleaching is continued at a pH below 4.5 to achieve an increased brightness of the bleached pulp compared to a similar bleach without carbon dioxide.

It has been found that the initial reactions are very rapid and that even a very short initial period provides a beneficial result on the bleaching. However, the initial period should preferably last at least one minute, more preferably 1 to 5 minutes.

The preferred way of adding the carbon is by injecting carbon dioxide in gaseous form

into the pulp suspension in a tank or a pipe of the plant. The carbon dioxide may, however, also be introduced in liquid or solid form.

The carbon dioxide is preferably fed directly into the aqueous pulp suspension. It may, however, also be added to an aqueous liquid, such as dilution water, which is fed to the suspension prior to the bleaching stage. For the purpose of the invention it is not critical how the carbon dioxide enters the suspension, it is only required that it will provide carbon dioxide in the aqueous pulp suspension.

The carbon dioxide should preferably be added directly to the pulp suspension prior to or in immediate connection to the bleaching stage in question, but after any washing stage, that might precede the bleaching stage. If added to the washing stage, most of the carbon dioxide will be removed with the washing water and the effect on the bleach will be inadequate.

Another preferred embodiment of the invention is to add carbon dioxide to the pulp suspension before a storage tower which precedes the chlorine dioxide stage in question.

Preferably said carbon dioxide comprises gaseous carbon dioxide which is injected into a flowing stream of said pulp suspension just prior to the addition of the chlorine dioxide bleaching agent. A preferred addition point for the carbon dioxide is in a pipe right after a pump to provide an adequate mixing of the carbon dioxide into the pulp stream.

The use of carbon dioxide for providing a desired pH profile in accordance with the present invention has a number of advantages, e.g.:

- an improved brightness and decreased kappa number of the pulp may be obtained as the carbon dioxide will retain a high pH in the initial bleaching period,
- the improved bleaching action may be used for reducing the consumption of bleaching chemicals and/or increasing the final pulp brightness,
- by providing a buffering system based on carbon dioxide, the balance between sodium and sulfur is not affected when spent liquor from the chlorine dioxide stage is recycled to the chemical recovery cycle,
- carbon dioxide initially acts as an acid, but is still non-corrosive for piping and other equipment,
- acidification without sulfur reduces the sulfur load in the recovery cycle of the mill,
- handling of carbon dioxide in the plant is technically uncomplicated,
- there are no environmental hazards associated with carbon dioxide.

The pulp suspension to be treated according to the present invention may be a chemical pulp, such as a sulfate, sulfite, soda, polysulfide, anthraquinone, polysulfide-anthraquinone pulp or a so called organosolv pulp, i.e. a pulp produced by adding an organic solvent during the main delignification (cooking) stage. The pulp may also be a mechanical pulp, a chemi-mechanical pulp, a semi-chemical pulp, a pulp containing recycled fibers or broke. Other pulp types can also be bleached with the use of carbon dioxide in accordance with the present invention and the pulp to be treated may be a mixture of any of the above pulp types.

The pulp may be introduced into the bleaching plant after cooking or it may be directed to the bleaching plant via an oxygen delignification stage and possibly other treatments.

The consistency of the pulp may be in the low, medium or high consistency range. For better handling it is generally preferable to use a low or medium consistency pulp. A typical consistency is 1 to 18%, preferably 3 to 15%.

The present invention also includes the processing of the bleached pulp further in a pulp or paper mill to provide dried pulp and/or paper containing said bleached pulp. The production of dried pulp and paper from the bleached pulp can be performed in the conventional way which is well known to those skilled in the art.

The present invention also relates to the use of carbon dioxide in the chlorine dioxide bleaching of an aqueous lignocellulosic pulp suspension for providing in said suspension a buffering system capable of retarding the decrease in the pH of said cellulosic pulp suspension caused by an addition of chlorine dioxide to said suspension, in order to provide an initial chlorine dioxide bleaching period at a $\text{pH} \geq 4.5$, the buffering capacity of said system being consumed after said initial period by acidic reaction products generated in said suspension and causing the pH to drop to a value below 4.5 after said initial period.

The invention will now be described in some detail with reference to the enclosed drawing, wherein

Figs 1 to 4 show pH profiles obtained in trials with and without the use of carbon dioxide in accordance with the present invention.

The pulp suspension entering a bleaching plant is generally alkaline which facilitates the dissolution of carbon dioxide in the pulp suspension. When carbon dioxide is added to an

alkaline pulp suspension the pH of the suspension is decreased. However, sometimes it may be more suitable to adjust the pH of said pulp by the use of another acid. It is conventional in the art to acidify the pulp by sulfuric acid either before chlorine dioxide addition or in combination with the feeding of chlorine dioxide in order to control the final pH. Such a practice is suitable also in the working of the present invention, if desired.

Other acids which are suitable for use as additional acidifying agents before the bleaching treatment are exemplified by sulfurous acid and waste acid from the chlorine dioxide production, etc. The pH may also, if needed, be adjusted with bases, such as sodium hydroxide, oxidized white liquor, totally oxidized white liquor, etc. The bases are preferably added to the pulp suspension before or in connection with the addition of the carbon dioxide.

It should be noted that carbon dioxide is an environmentally much more acceptable chemical than most other acids. Therefore using carbon dioxide alone is the preferred procedure from an environmental point of view. Moreover, it should be noted that in the present invention carbon dioxide added to the solution at the beginning of the bleaching stage may even leave the solution by the end of the bleaching stage when the pH has dropped to its lower value.

The carbon dioxide provides its buffering action via a system of bicarbonate ions in the solution. The buffering system is thus created without the addition of other chemicals which might have a negative impact on the overall process. Thus, for instance, the balance between sulfur and sodium in the recovery of chemicals will not be affected by the carbon dioxide.

In the working of the present invention, the final acidic pH below 4.5 in the bleaching stage is provided by the reaction of the bleaching agent with the components of the lignocellulosic pulp. The products of these reactions are partly acidic in nature and will, after the initial high pH period ($\text{pH} \geq 4.5$) created by the addition of carbon dioxide, overrun the buffering action provided by the carbon dioxide buffering system. As the pH drops below pH 4.5 the balance in the carbon dioxide dissociation equilibrium moves towards a regeneration of carbon dioxide, as described above. The regenerated carbon dioxide may leave the suspension at the low pH or may remain in the aqueous phase. However, at the low pH there exists only a minimal amount of bicarbonate ions in the system and the buffering system has lost its buffering capacity.

In the working of the present invention the initial pH of the alkaline pulp may be lowered

with carbon dioxide to near neutral. The added chlorine dioxide is used so as to obtain the desired final pH of about 1.7 to 4.4 taking into account the acidic byproducts of the bleaching reactions. It is to be noted that although the carbon dioxide addition provides an initial lowering of the pH, its pH lowering effect is lost at the low final pH. In actual fact, the addition of carbon dioxide may increase the final pH obtained with a certain chlorine dioxide dosage.

It is obvious to those skilled in the art that the present invention forms an improvement in a conventional process in a pulp mill and that the final product of the process is paper or pulp bleached according to the described invention. Consequently, the present invention also concerns a process for producing paper or pulp from the pulp suspension bleached according to the present invention. Processing of said bleached pulp may include conventional extraction, delignification and/or bleaching steps in the bleaching plant, as well as the conventional procedures performed for forming a web of paper or pulp in a web forming part of the mill. Such procedures are well known to those skilled in the art and are therefore not disclosed here in any detail.

The invention will now be described in greater detail with the aid of some examples which are only illustrative and which should not be construed as limiting the invention in any way.

Examples

Chlorine dioxide bleaching trials (D0), were performed in a laboratory Quantum mixer. An oxygen delignified softwood pulp with kappa number 12 was used. In those trials where the pulps were pH adjusted, H_2SO_4 was added before the pulps were placed in the mixer. CO_2 gas was added to the pulp in the mixer under application of slow stirring.

Chlorine dioxide was placed in a dosage container and added to the mixer by using compressed air. The pH was monitored during the bleaching time of 60 minutes. The temperature in the mixer was between 45-50°C. After the bleaching, the pulp was washed with deionized water. Filtrate from the chlorine dioxide stage was analysed for residual chlorine.

Thereafter the pulps were alkaline extracted (E) for 1 hour at 70 °C. The alkaline extraction was performed in a plastic bag placed in a temperature-controlled water bath. The brightness and kappa number of the pulp was measured after D0 E.

The results of the trials are shown in the Table below and in the appended Figs 1 to 4.

Run No.	Charge kg/t			pH		Consumed ClO_2 kg act/t	Kappa Number	Brightness %ISO
	CO_2	H_2SO_4	ClO_2 as act. Cl	after 4 min.	after 60 min.			
1	0	0	18	5.4	5.5	14.4	7.2	48.7
2	0	2	18	3.9	3.2	17.4	5.2	55.8
3	0	6	18	2.9	2.8	17.8	6.4	54.7
4	3.5	0	18	4.8	4.4	17.0	4.8	59.4
5	0	1.5	18	4.2	3.7	17.8	5.6	58.1
6	2.5	0	30	4.8	3.4	29.3	2.8	63.5
7	0	3	30	4.0	3.0	29.7	4.0	58.4
8	2.5	1	30	5.0	4.1	29.0	3.7	60.9
9	0	1	30	4.2	3.0	29.7	3.8	60.9

In the first three runs, the pulps were pH adjusted with varied charges of H_2SO_4 . The charge of chlorine dioxide was 18 kg active chlorine/ton of pulp. In the first run the pH was kept at too high a level and the desired bleaching reactions did not take place. A large share of the added chlorine dioxide remained in the filtrate after the bleaching. The pulp had a significantly lower brightness and higher kappa number after D0 E, compared to runs No. 2 and 3.

In run No. 3 the charge of H_2SO_4 was higher than in runs 1 and 2, which resulted in that the pH dropped to 2.9 already after 4 minutes. In spite of the low residual chlorine in the filtrate after D0, the bleachability of the pulp was low. The result shows that the pH during the bleaching stage (especially the first minutes) is just as important as the final pH. (See Fig. 1 for the pH profiles)

In run No. 4, CO_2 was added to the pulp, which kept the pH above 4.5 during the first 4 minutes. Compared to run No. 5, the consumed active chlorine was reduced with 0.8 kg/t at the same time as the brightness increased by 1.3 units and the kappa number decreased by 1 unit. (See Fig. 2 for the pH profiles)

In runs 6-9, the chlorine dioxide charge was increased to 30 kg active chlorine/ton of pulp. The CO_2 charge in run No. 6 resulted in that the pH remained above 4.5 during the initial bleaching. The brightness was increased by 5 units at the same time as the chemical consumption was reduced compared to run No. 7 without CO_2 addition. The optimal final pH was lower for D0-stages with a high charge of chlorine dioxide. With CO_2 addition the optimal final pH seemed to be higher. (See Fig. 3 for the pH profiles)

In runs No. 8 and 9, the pulps were adjusted to the same initial pH with H_2SO_4 . CO_2 was

then added to run No. 8. The brightness results were the same in the two runs, even though the consumption of chlorine dioxide was reduced by 0.7 kg active chlorine/per ton of pulp in the run with CO₂ addition. (See Fig. 4 for the pH profiles)

The brightness of the pulp in run No. 9 was higher than the pulp in run No. 7 even though the final pH was the same. This again indicates the importance of the pH in the beginning of the chlorine dioxide stage, which is somewhat higher in run No. 9.

The tests clearly show that the addition of carbon dioxide provides a beneficial pH profile to the bleaching with chlorine dioxide.

The above trials are examples of bleaching performance and they are not intended to represent the best or the only way to perform the chlorine dioxide bleaching of the present invention.

The present invention is not limited to the exact disclosure of the invention as described above. The person skilled in the art will be able to perform such modifications and applications which are common in the art without deviating from the scope of the appended claims.

Claims

1. A process for bleaching a lignocellulosic pulp with chlorine dioxide in an aqueous suspension at different pH values, said process comprising the following stages:

providing an aqueous lignocellulosic pulp suspension in a first chlorine dioxide bleaching stage after cooking,

adding carbon dioxide to said lignocellulosic pulp,

subsequently adding a chlorine dioxide bleaching agent to said lignocellulosic pulp suspension,

said carbon dioxide being added for providing in said suspension a buffering system capable of retarding the decrease in the pH of said cellulosic pulp suspension after said addition of chlorine dioxide in order to provide an initial chlorine dioxide bleaching period at a $\text{pH} \geq 4.5$, the buffering capacity of said system being consumed after said initial period by acidic reaction products generated in said suspension and causing the pH to drop to a value below 4.5 after said initial period,

and subsequently continuing said chlorine dioxide bleaching at a pH below 4.5 and thereby achieving an increased brightness of the bleached pulp compared to a similar bleach without carbon dioxide.

2. A process according to claim 1, wherein the duration of said initial period is at least one minute, preferably 1 to 5 minutes.

3. A process according to claim 1 or 2, wherein said buffering capacity is lost due to a component of said buffering system reverting to another chemical and/or physical form.

4. A process according to claim 3, wherein carbon dioxide is regenerated in the aqueous and/or gaseous phase in said suspension as said buffering capacity is lost.

5. A process according to claim 1, wherein said carbon dioxide is added in gaseous, liquid, aqueous or solid form.

6. A process according to claim 5, wherein said carbon dioxide is fed to said pulp

suspension in a tank or a pipe or into a liquid to be added to said pulp prior to said chlorine dioxide addition.

7. A process according to claim 5 or 6, wherein gaseous carbon dioxide which is injected into a flowing stream of said pulp suspension just prior to the addition of said bleaching agent.
8. A process according to any one of the preceding claims 1 to 7, wherein the amount of carbon dioxide is adjusted so as to cause the buffering capacity of said buffering system to be consumed after a suitable length of said initial period by the acidic reaction products formed due to the action of the chlorine dioxide on said pulp.
9. A process according to any one of the preceding claims 1 to 8, wherein said aqueous cellulosic pulp suspension comprises a chemical pulp, an organosolv pulp, a mechanical pulp, a chemi-mechanical pulp, a semi-chemical pulp, a pulp containing recycled fibers or broke, or a mixture of any of these in a bleaching plant of a pulp mill.
10. A process according to claim 1, wherein said aqueous cellulosic pulp suspension comprises oxygen delignified pulp.
11. A process according to claim 1, wherein said aqueous cellulosic pulp suspension has a concentration of 1 to 18%.
12. A process according to claim 1, wherein the temperature at said chlorine dioxide bleaching is between 35°C and 105°C, preferably between 45°C and 75°C.
13. A process according to claim 1, wherein said pulp suspension after said chlorine dioxide bleaching is processed into bleached paper or pulp.
14. A process according to claim 13, wherein said processing includes an alkaline treatment.
15. A process according to claim 13 or 14, wherein said processing includes an oxygen delignification step and/or an extraction step.
16. Use of carbon dioxide in the chlorine dioxide bleaching of an aqueous lignocellulosic pulp suspension for providing in said suspension a buffering system capable of retarding the decrease in the pH of said cellulosic pulp suspension caused by an addition of chlorine

dioxide to said suspension, in order to provide an initial chlorine dioxide bleaching period at a $\text{pH} \geq 4.5$, the buffering capacity of said system being consumed after said initial period by acidic reaction products generated in said suspension and causing the pH to drop to a value below 4.5 after said initial period.

pH profile in D0
(kappa no. 12, 18 kg acL Cl/L, 45 °C, 60 min.)

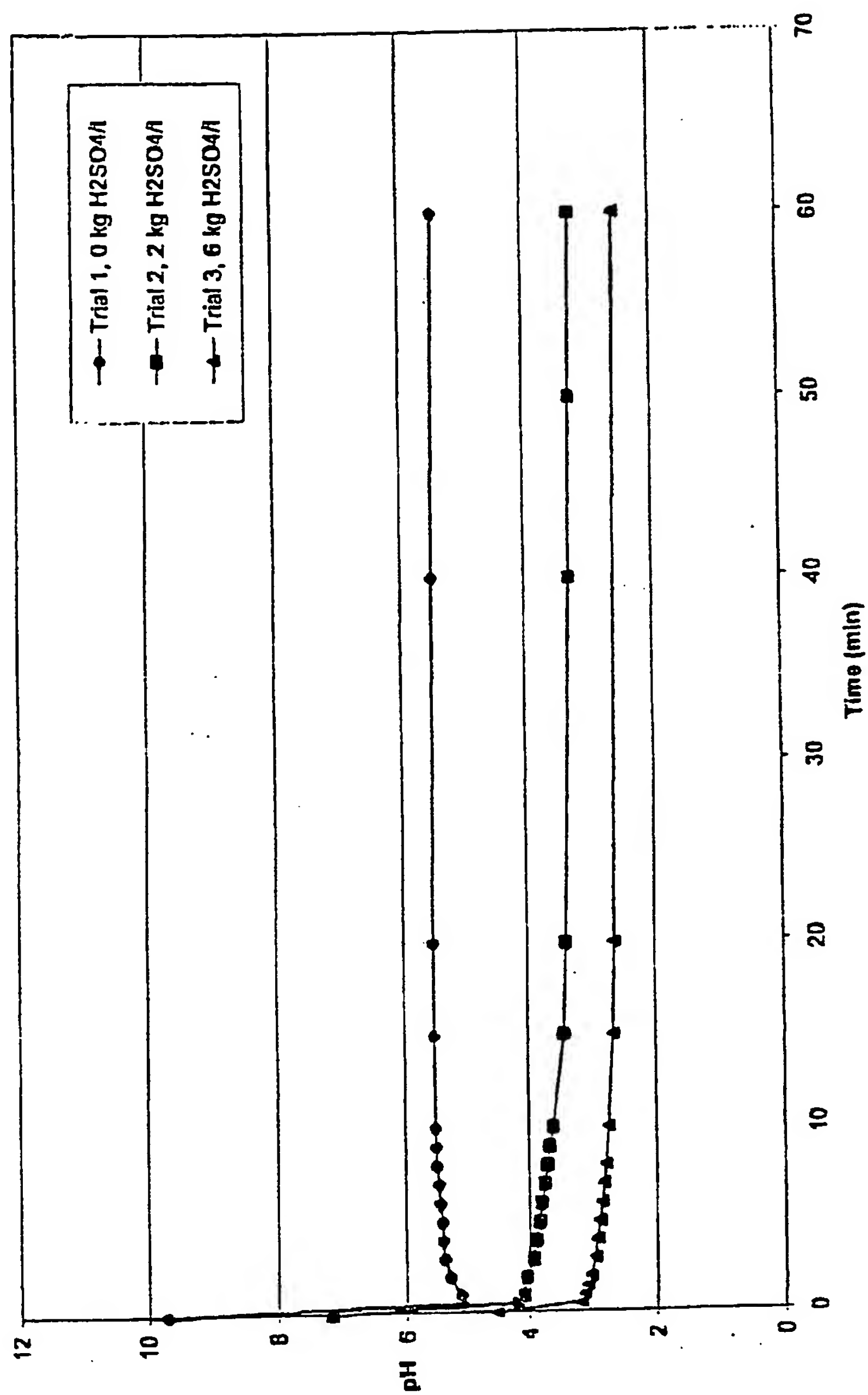


FIG. 1

pH profile in D0,
(kappa no. 12, 18 kg a.c.L Cl/L, 45 °C, 60 min.)

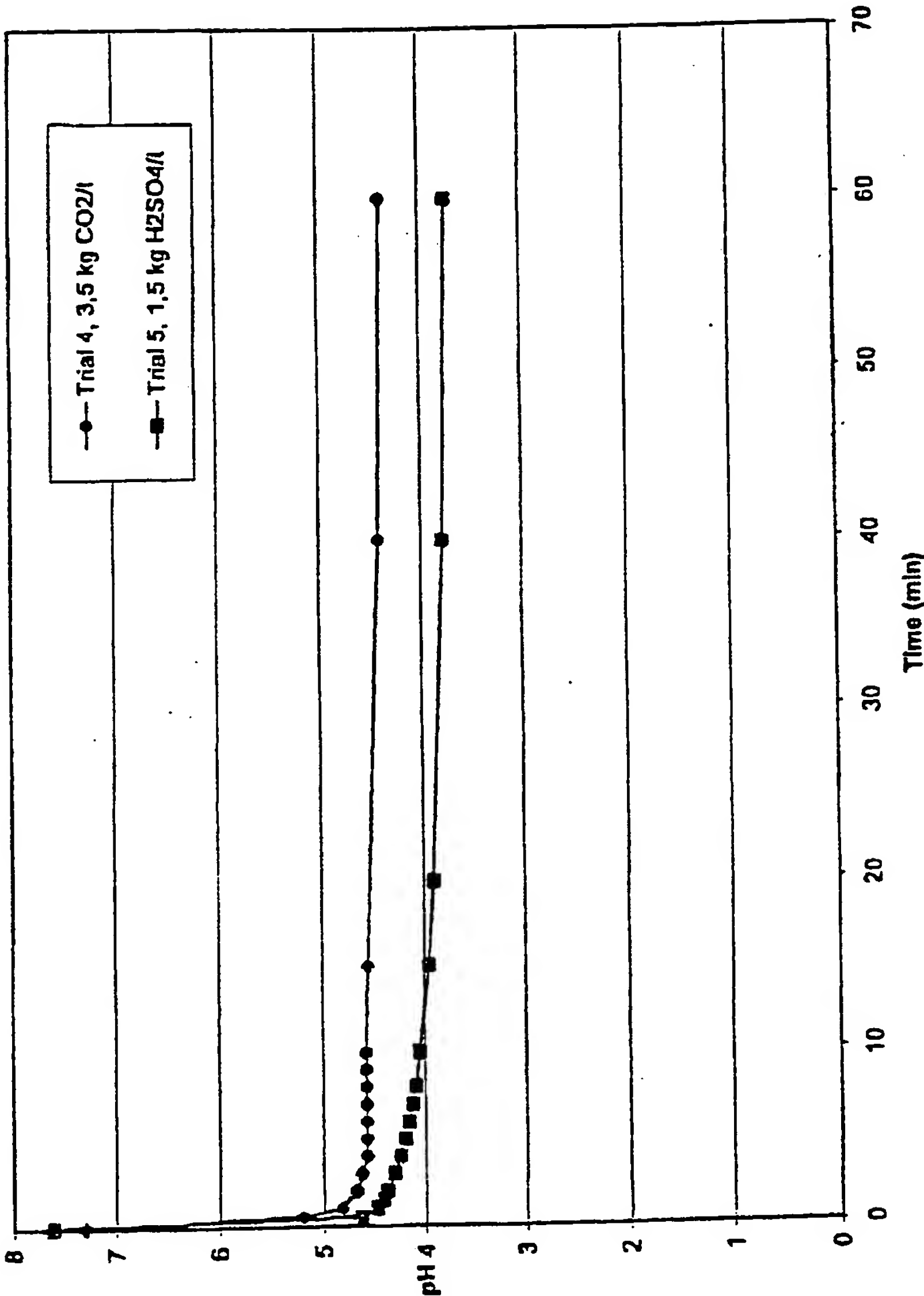


FIG. 2

pH profile in D0,
(kappa no. 12, 30 kg act Cl/l, 45 °C, 60 min.)

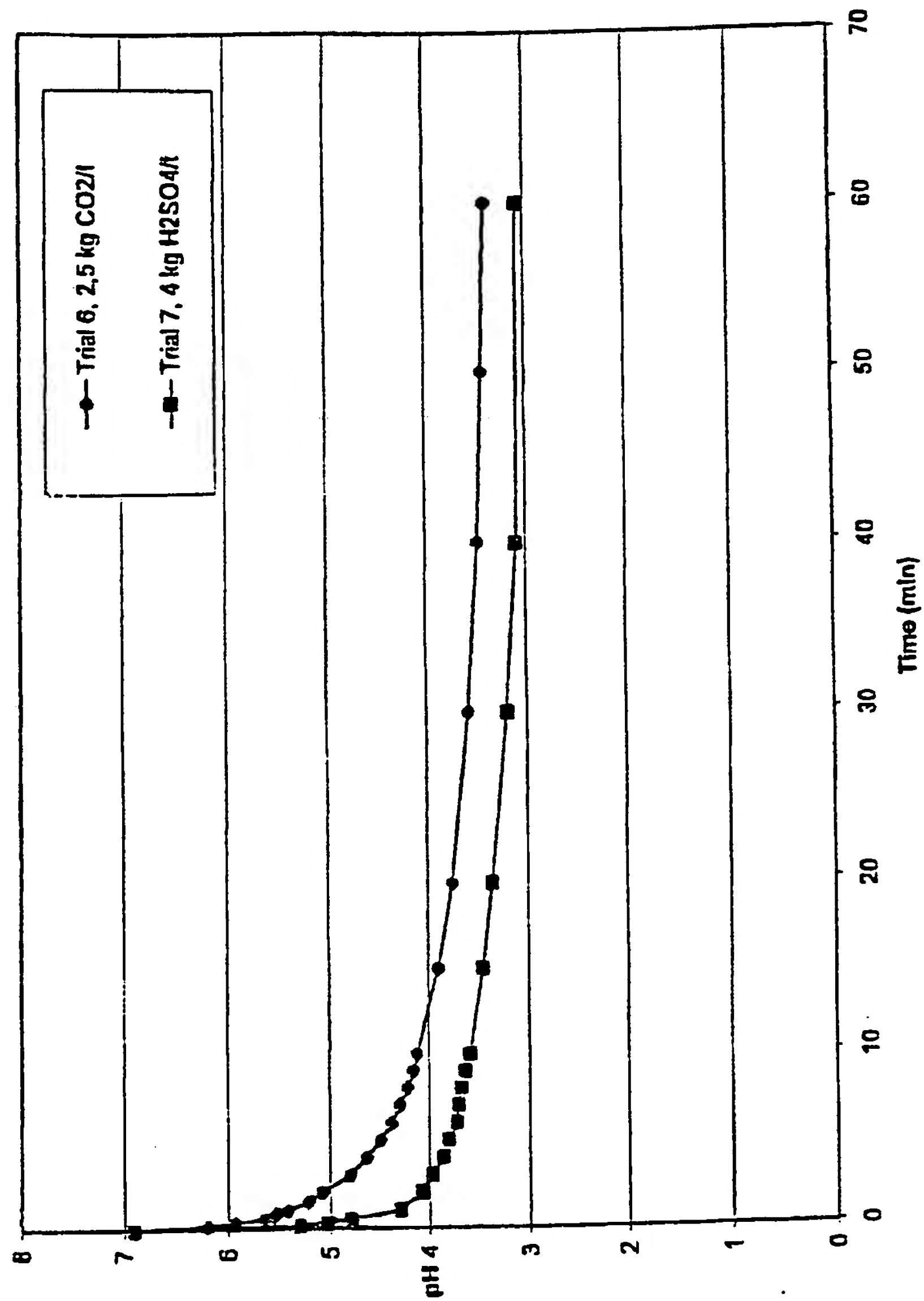


FIG. 3

pH profile in D0,
(kappa no. 12, 30 kg act Cl/l, 45 °C, 60 min.)

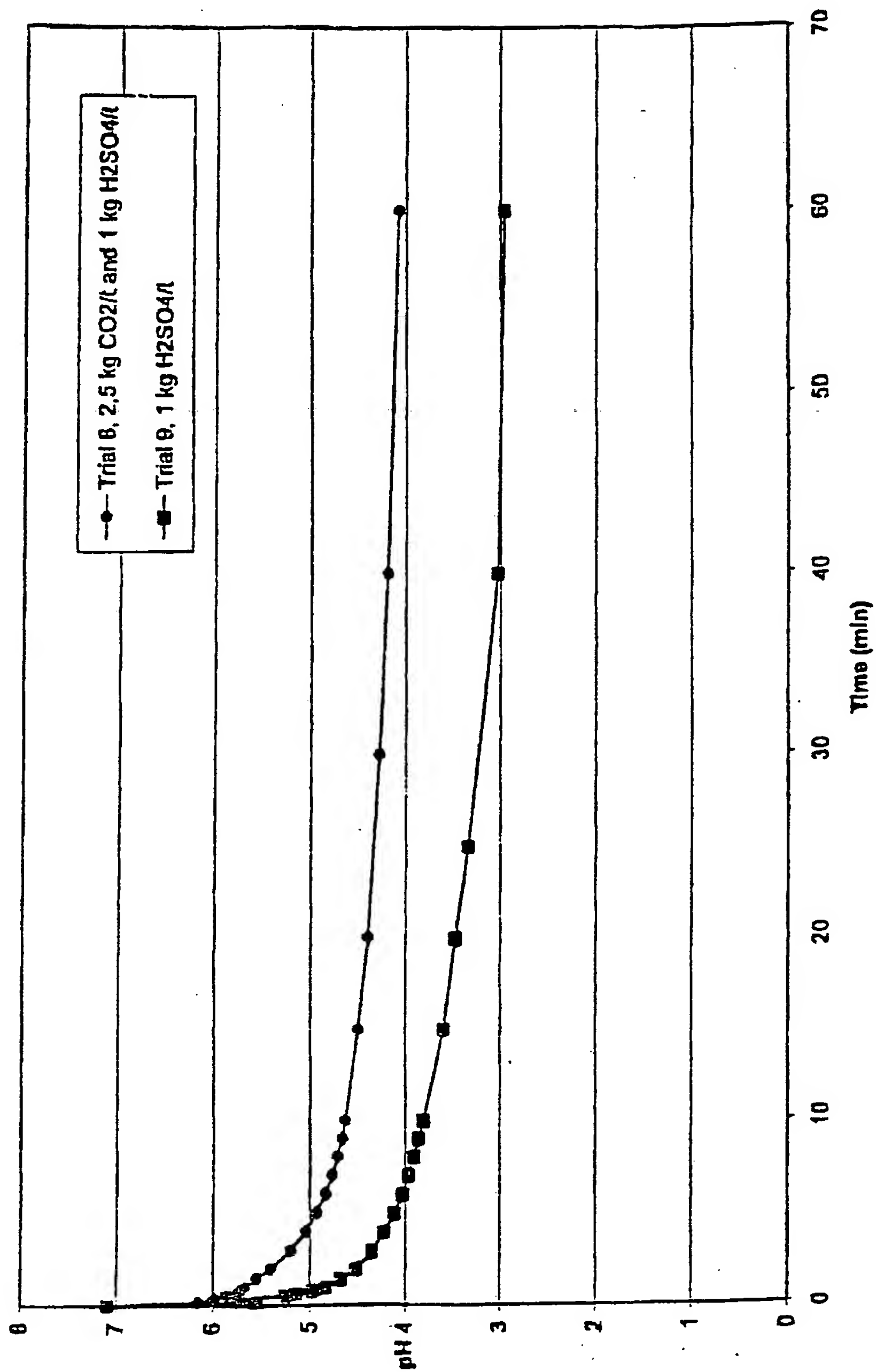


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/04067

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21C9/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 815 247 A (COLUMBIA CELLULOSE COMPANY LTD) 24 June 1959 (1959-06-24) page 2, line 16 - line 41	1-16
Y	EP 0 899 374 A (OJI PAPER CO) 3 March 1999 (1999-03-03) page 4, line 26 - line 51 claims 1,2,8	1-16
Y,P	WO 00 73576 A (AGA AB ;TIGERSTROEM ANNA (SE)) 7 December 2000 (2000-12-07) claims 2,14	1-16
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	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *8* document member of the same patent family

Date of the actual completion of the international search

28 August 2001

Date of mailing of the international search report

10/09/2001

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INTERNATIONAL SEARCH REPORT

Internat. Application No.
PCT/EP 01/04067

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	SEGER ET AL. (SEGER, G., JAMEEL, H., CHANG, H-M.): TAPPI JOURNAL, no. 7, pages 174-180, XP002175204 cited in the application abstract	1-16

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